Journal of the European Ceramic Society 38 (2018) 3539–3546

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Theoretical exploration of the abnormal trend in lattice thermal conductivity for monosilicates RE_2SiO_5 (RE = Dy, Ho, Er, Tm, Yb and Lu)

Yiran Li[a,b], Yixiu Luo[a,c], Zhilin Tian[a,b], Jiemin Wang[a], Jingyang Wang[a,*]

[a] High-performance Ceramics Division, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, China
[b] University of Chinese Academy of Sciences, Beijing, 100049, China
[c] University of Science and Technology of China, Hefei, 230026, China

ARTICLE INFO

Keywords:
Environmental barrier coating
Rare earth silicate
Thermal conductivity
Phonon anharmonicity
First-principles calculation

ABSTRACT

Rare earth monosilicates RE_2SiO_5 have been considered as promising environmental barrier coating materials for silicon-based ceramics due to their low thermal conductivity and good high-temperature stability. We herein performed a systematic study of the lattice dynamics for RE_2SiO_5 (RE = Dy, Ho, Er, Tm, Yb and Lu) using first-principles calculations. The loosely bound rare earth atoms provide large Grüneisen parameters and low phonon group velocities, both of which determine the low thermal conductivity. Theoretical exploration predicts an anomalous increase of lattice thermal conductivity with increment of RE atomic number and the mechanism is explained by the stronger atomic bonding and weaker phonon anharmonicity. Although incorporating heavier atoms has long been considered as an effective way to reduce lattice thermal conductivity, this work addresses the importance of bonding heterogeneity and anharmonicity rather than atomic mass variation. This theoretical study suggests an alternative approach towards the design of new thermal insulating materials.

1. Introduction

Silicon-based ceramics, such as silicon carbide (SiC), monolithic silicon nitride (Si_3N_4) and their ceramic matrix composites (CMCs), exhibit superior strength and reliability at elevated temperature, indicating their potential to bring a breakthrough in gas turbine engine performance. The development of silicon-based ceramics will promote gas turbine engine technology significantly [1]. However, a major barrier to realizing silicon-based ceramic turbine is their weakness of environmental durability in combustion environments containing water vapor [2–4]. To prevent this high recession rate of silicon-based ceramics, environmental barrier coatings (EBCs) are promising for protection of turbine engines from water vapor corrosion, improvement of hot section service temperature and increment of durability in combustion environments [5–7].

Scientists have focused on screening in solid candidates and developing preparation technology for decades. Recently rare earth (RE) silicates are recognized as the third generation of EBC materials because of their excellent thermochemical and thermal expansion compatibility with silicon-based matrix. Prime among them are the RE monosilicates RE_2SiO_5 (RE = Dy, Ho, Er, Tm, Yb and Lu) with *C12/c1* space group, which are attracting considerable interests for their low thermal conductivity, ultralow steam volatility and good high-temperature stability [8–13]. Since one of the primary requirement for EBC design is low thermal conductivity, lots of efforts are currently concentrated on investigating thermal properties and reducing thermal conductivities of EBC candidates. Recently Tian et al. [14] reported very low experimental thermal conductivities of RE_2SiO_5 and predicted an increase of lattice thermal conductivity with atomic number of RE element based on theoretical explorations of elastic and thermal properties. Although several studies have been devoted to characterize thermal properties of RE_2SiO_5 in experiment [12,14,15], the physical origin of their low thermal conductivity and the underlying mechanism of the trend in lattice thermal conductivity are much less studied.

Motivated by these considerations, a systematic study of the lattice dynamics of RE monosilicates RE_2SiO_5 (RE = Dy, Ho, Er, Tm, Yb and Lu) was done using first-principles and lattice dynamics calculations. A rigorous analysis of equilibrium structures, atomic interactions, phonon dispersions, vibration modes, Grüneisen parameters and phonon relaxation time help us build a clear profile of the phonon behaviors in RE_2SiO_5. Theoretical exploration predicts an anomalous increase of lattice thermal conductivity in RE_2SiO_5 with a higher RE atomic number. Nature of the increased thermal conductivity is disclosed as the stronger atomic bonding and weaker phonon anharmonicity. In

* Corresponding author.
E-mail address: jywang@imr.ac.cn (J. Wang).

https://doi.org/10.1016/j.jeurceramsoc.2018.04.014
Received 31 October 2017; Received in revised form 30 March 2018; Accepted 7 April 2018
Available online 12 April 2018

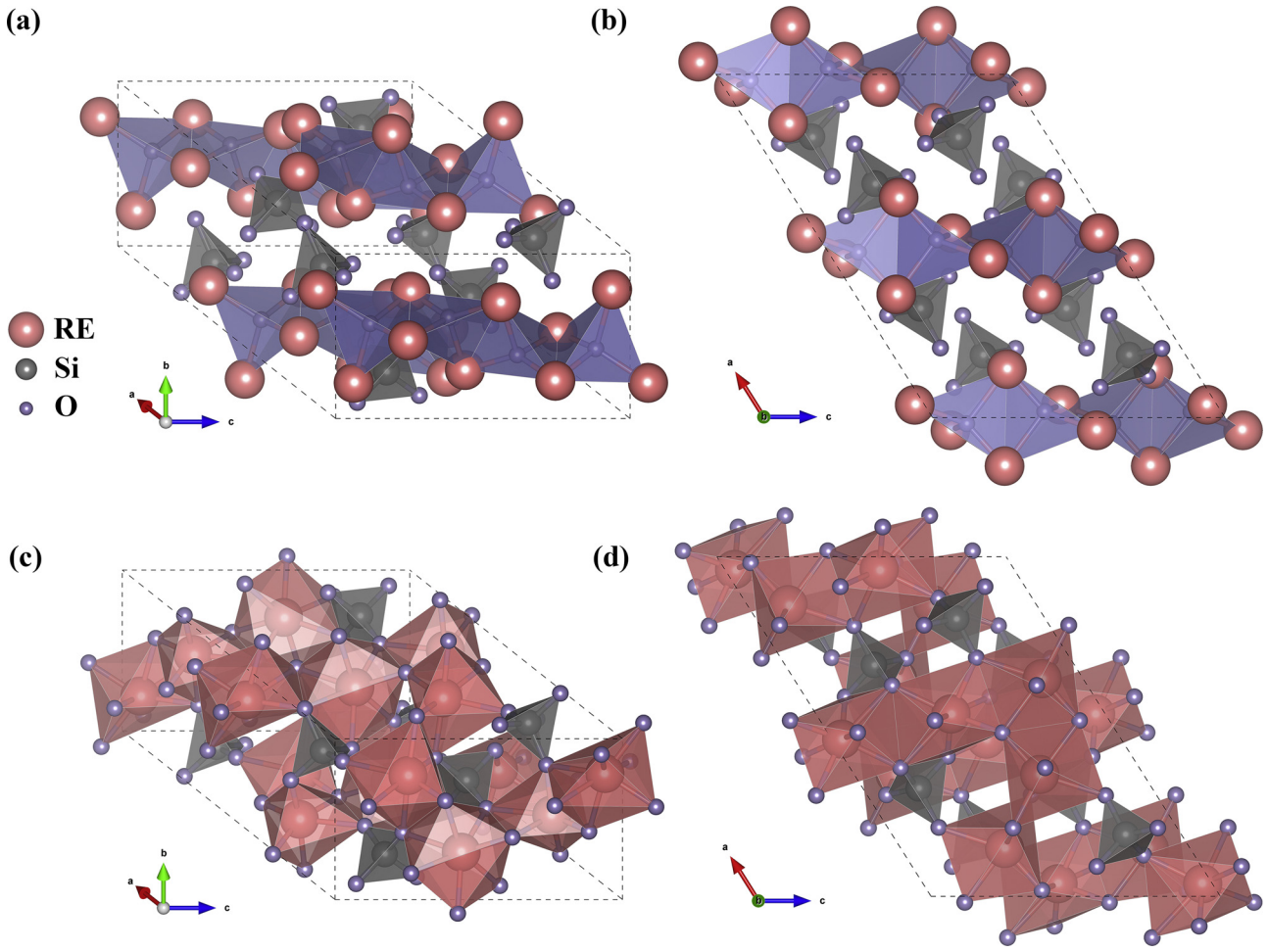

Fig. 1. (a) and (c) Crystal structure of RE_2SiO_5 and (b) and (d) its projection along the *c* axis.

addition, loosely bound RE atoms are found to provide large Grüneisen parameters and small phonon group velocities, both of which determine the low thermal conductivity of the set of RE_2SiO_5. This theoretical study presents clear information on the phonon behaviors in RE_2SiO_5 and suggests practical guideline towards the design of new thermal insulating candidates including environmental barrier coatings.

2. Computational details

We did density functional theory (DFT) [16] calculations using the Vienna Ab initio Simulation Package (VASP) computational code [17]. The electronic exchange-correlation functional was described with the Perdew-Burke-Ernzerhof (PBE) approximations of the generalized gradient approximation (GGA) [18]. The projector-augmented wave (PAW) [19] treatment with energy cutoff of 750 eV was used. Valence electrons $5p^6 5d^1 6s^2$ for RE atoms, $3s^2 3p^2$ for Si and $2s^2 2p^4$ for O were adopted in PAW potentials. The *f* electrons of RE atoms were frozen into the core states. The electronic Brillouin zones were sampled with a $3 \times 3 \times 3$ Monkhorst-Pack k-mesh [20]. Lattice constants and internal atomic coordinates were fully relaxed. Electronic optimizations and structural optimizations were carried out using a total energy convergence criterion of 1.0×10^{-8} eV/atom.

Lattice dynamics calculations were carried out through the finite-displacement method using the PHONOPY package [21]. A supercell with dimension of $1 \times 2 \times 1$ and with displacement size of 0.01 Å was used for RE_2SiO_5 to prevent fictitious interactions. As an instance, the lengths of as-used supercell are 14.269 Å, 13.334 Å and 10.280 Å for Lu_2SiO_5. The second-order pairwise interatomic force constants (IFCs) were obtained using VASP code.

In particular, the mode Grüneisen parameters were obtained by calculating phonon frequencies for the isotropically expanded (compressed) structures whose volumes were changed by +3% (−3%). Hence, mode Grüneisen parameter $\gamma(\mathbf{q}i)$ at the wave vector $\mathbf{q}$ with band index i was calculated by:

$$\gamma(\mathbf{q}i) = -\frac{V}{\omega(\mathbf{q}i)}\frac{\partial\omega(\mathbf{q}i)}{\partial V} = -\frac{V}{2[\omega(\mathbf{q}i)]^2}\left\langle e(\mathbf{q}i)\left|\frac{\partial D(\mathbf{q})}{\partial V}\right|e(\mathbf{q}i)\right\rangle \quad (1)$$

Here, V is the volume, $\omega(\mathbf{q}i)$ is the phonon frequency, $D(\mathbf{q})$ is the dynamical matrix, and $e(\mathbf{q}i)$ is the eigenvector. Accordingly, overall Grüneisen parameter γ_{all} is the average of the mode Grüneisen parameter $\gamma(\mathbf{q}i)$ weighted with the contribution of each mode to lattice specific heat $C(\mathbf{q}i)$:

$$\gamma_{\text{all}} = \left(\frac{\sum_{\mathbf{q}i}\gamma^2(\mathbf{q}i)C(\mathbf{q}i)}{\sum_{\mathbf{q}i}C(\mathbf{q}i)}\right)^{1/2} \quad (2)$$

$$C(\mathbf{q}i) = \frac{(\hbar\omega(\mathbf{q}i))^2}{k_B T^2}\cdot\frac{\exp(\hbar\omega(\mathbf{q}i)/k_B T)}{[\exp(\hbar\omega(\mathbf{q}i)/k_B T)-1]^2} \quad (3)$$

Acoustic Grüneisen parameter γ_{acoustic} is also defined by Eq. (2) but summation runs over the modes whose energies are lower than the highest acoustic frequency.

Lattice thermal conductivity is calculated by Slack model [22]:

$$\kappa_L = \frac{B_\gamma M_a \delta\theta_D^3}{N_{\text{cell}}^{2/3}\gamma^2 T} \quad (4)$$